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54 **Flexible laminated fluoropolymer containing composites.**

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## Description

### Background of the Invention

5 This invention relates to flexible fluoropolymer-containing composites, to a method of making the composites by film lamination techniques, and to protective garments and other articles made from such novel composites, as well as to a method for making such articles. Articles made with composites according to this invention are chemically resistant and the composites are sufficiently flexible to permit fabrication of protective garments. Fire resistant composites can also be made.

10 Protective garments are currently available which provide some measure of chemical protection. These garments can be made from non-woven spun-bonded polyethylene (Tyvek) or polyester (Sontara), and from laminates of Tyvek with polyethylene or Saran. Other materials, such as butyl or neoprene elastomers, fluoroelastomers and chlorinated polyethylene can also be used in protective garments. For example, U.S. Patents Nos. 4,421,878 and 4,423,183 teach that cured fluoroelastomer films (Viton) may be useful as a  
 15 coating in safety apparel. Each of these materials, however, is permeable to or degraded by some classes of chemicals. They are not resistant to the complete spectrum of toxic and hazardous materials potentially encountered in hostile environments. Moreover, garments of these materials require flame resistant oversuits where both chemical and fire protection are necessary. Elastomeric materials, such as Viton or butyl rubber, are irreversibly contaminated by some hazardous materials, such as nitrobenzene and cannot  
 20 be cleaned. Furthermore, the barrier properties of these materials are detrimentally affected by decontamination, and therefore articles made of these materials are not suitable for reuse.

U.S. Patent No. 4,165,404 describes a process for producing coated laminates of knit or woven fabrics with a thick fluorinated copolymer sheet using an interlayer of low melt viscosity copolymer. The composites thus formed are not sufficiently flexible for use as garments, and are so structured as to be  
 25 specifically suitable for molding rigid articles.

Fire resistant protective garments have been made from spun-laced Nomex. These materials have no chemical resistance, however, due to the open structure of the fabric. Previous efforts at coating Nomex spun-laced fabrics to achieve a material which is both chemical and fire resistant have resulted in loss of the flexibility necessary for clothing.

30 CH-A-522502 pertains to a multi-layer sheeting which, when cut into individual pieces, is suitable for covering a variety of subjects. The sheeting is particularly useful as a protective cover for automobiles and machinery. The multi-layer sheeting consists of several thin polyesters or polyester-like films where, between the individual films, there is an inner layer and adhesive. The nature of the inner layer allows the adhesive to penetrate through it which causes all components to bond together.

35 BE-A-651049 relates to packaging which may comprise a variety of components including fluoropolymer components, but all components must be biaxially oriented or metallized, unlike the present invention. The fluoropolymer is not disclosed as having any adhesive property.

GB-A-2 074 941 relates to a flexible mat structure incorporating a metal wire or synthetic yarn covered with a plastic or elastomer material impervious to gases or liquids. None of the materials disclosed in the  
 40 patent application at issued is disclosed in this British patent.

GB-A-977 367 relates specifically to a technique for joining together pieces of fabric having thermoplastic coatings.

Accordingly, it is an object of the present invention to provide flexible composites which may be resistant to both fire and hazardous materials for use in protective garments and other articles such as  
 45 covers and shelters. Fire resistant materials can be obtained using a fire resistant flexible substrate.

It is a further object of this invention to provide a method for seaming materials having a melt adhesive on both sides. This method uses heat sealed seams, or a combination of sewing and heat sealing. In the latter case, the sewn seam is never exposed to the challenge agent.

### 50 Brief Summary of the Invention

A flexible and resistant composite is formed by laminating a thin fluoropolymer-containing film to on or both sides of a flexible substrate suitable for use as a garment, shelter or covering. The film component, or components where both sides of the substrate are laminated, are preferably each less than 5 mils thick.  
 55 The film components according to the invention are suitable to provide the desired barrier properties at minimal thicknesses. Any adhesive used to join the laminate may be applied to either the substrate, or the fluoropolymer-containing film. Application of the adhesive to the film avoids permeation of nonwoven substrates to enhance the flexibility of the composites formed without diminishing the chemical resistance

or barrier properties. The resulting material has good cohesive strength, and is highly flexible. When two layers of fluoropolymer are used, one on each side of the substrate, greatly increased chemical resistance is obtained. The composite materials produced according to the present invention are resistant to a broad spectrum of hazardous chemicals: volatile organics; organic and inorganic acids and bases; volatile solids; and inorganic and organic salts in solution.

The material of the present invention is well suited to the making of protective garments, such as hoods, coveralls, supplied-air suits, gloves, and footwear. The material is also suitable for use in respirators or other equipment, tents or other shelters, and in any other application where flexible, fire and chemical resistant materials are needed.

#### Detailed Description of the Invention

According to the present invention, it is provided 2 flexible protective article made of a composite comprising a protective layer laminated to one or both sides of a flexible substrate, said layers being less than 127 micrometers (5mil) thick and an adhesive applied between the protective layers and the flexible substrate, characterized in that the protective layer is a fluoropolymer containing layer and the adhesive is a melt bondable adhesive having a melt temperature lower than the substrate and the fluoropolymer-containing layers, and selected from the group comprising FEP, FEP alloyed with PTFE, PTFE and PFA.

According to another feature, the melt adhesive is between 0.00253 mm (0.1 mil) and 0.0381 mm (1.5 mil) thick.

According to another feature, the same fluoropolymer comprises both the protective layer as well as the adhesive. According to another feature, FEP comprises the protective layer as well as the adhesive.

These materials retain their flexibility or suppleness and show improved resistance to chemical permeation and degradation. The resistance to chemicals is unexpectedly pronounced when double sided laminates are used. The barrier properties of double-sided composites are substantially enhanced over those of single-sided composites with the same total film thickness. Moreover, materials according to the present invention are not irreversibly contaminated by chemicals like nitrobenzene as are some elastomeric materials, such as butyl rubber and Viton, and can be cleaned. The materials according to this invention do not show loss of barrier properties upon decontamination.

The fluoropolymer-containing film used according to the present invention contains a fluoroelastomer, a perfluoroelastomer, a fluoroplastic, a perfluoroplastic, or a blend of fluoro- or perfluoroelastomers and fluoro- or perfluoroplastics. The preferred fluoropolymer is a fluoroplastic, preferably polytetrafluoroethylene (PTFE). Moreover, the film may comprise a blend of a fluoropolymer and a polyimide, a polyamide-imide, or a polyphenylene sulfide.

The term "fluoroplastic" as used herein encompasses both hydrogen-containing fluoroplastics and hydrogen-free perfluoroplastics, unless otherwise indicated. Fluoroplastic means polymers of general paraffinic structure which have some or all of the hydrogen replaced by fluorine, including, *inter alia*, polytetrafluoroethylene (PTFE), fluorinated ethylene propylene (FEP) copolymer, perfluoroalkoxy (PFA) resin, homopolymers of polychlorotrifluoroethylene (PCTFE) and its copolymers with TFE or VF<sub>2</sub>, ethylene-chloro-trifluoro-ethylene (ECTFE) copolymer and its modifications, ethylenetetrafluoroethylene (ETFE) copolymer and its modifications, copolymers of TFE with pentafluoropropylene, polyvinylidene fluoride (PVDF), and polyvinylfluoride (PVF).

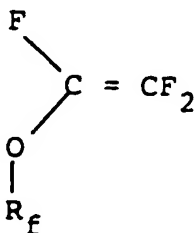
Similarly, the term "fluoroelastomer" as used herein shall encompass both hydrogen-containing fluoroelastomers as well as hydrogen-free perfluoroelastomers, unless otherwise indicated. Fluoroelastomer means any polymer with elastomeric behavior or a high degree of compliance containing one or more fluorinated monomers having ethylenic unsaturation, such as vinylidene fluoride, and one or more comonomers containing ethylenic unsaturation. The fluorinated monomer may be a perfluorinated mono-olefin, for example hexafluoropropylene, pentafluoropropylene, tetrafluoroethylene, and perfluoroalkyl vinyl ethers, e.g. perfluoro (methyl vinyl ether) or (propyl vinyl ether). The fluorinated monomer may be a partially fluorinated mono-olefin which may contain other substituents, e.g. chlorine or hydrogen. The mono-olefin is preferably a straight or branched chain compound having a terminal ethylenic double bond. The elastomer preferably consists of units derived from fluorine-containing monomers. Such other monomers include, for example, olefins having a terminal ethylenic double bond, especially ethylene and propylene. The elastomer will normally consist of carbon, hydrogen, oxygen and fluorine atoms.

Any fluoropolymer component may contain a functional group such as carboxylic and sulfonic acid and salts thereof, halogen, as well as a reactive hydrogen on a side chain.

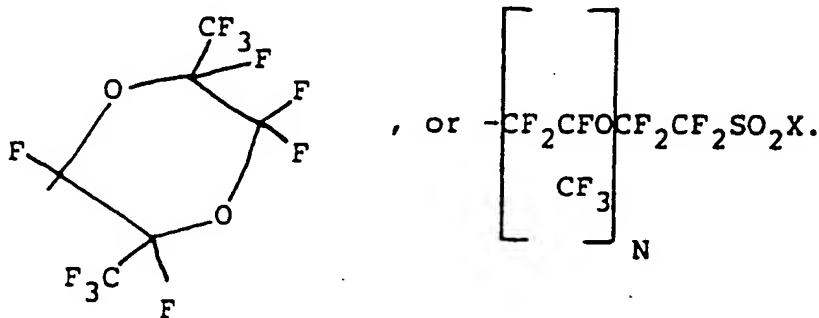
Preferred elastomers are copolymers of vinylidene fluoride and at least one other fluorinated monomer, especially one or more of hexafluoropropylene, pentafluoropropylene, tetrafluoroethylene and

chlorotrifluoroethylene. Commercially available fluoroelastomers include copolymers of vinylidene fluoride and hexafluoropropylene, such as Viton A, sold by DuPont; terpolymers of vinylidene fluoride, hexafluoropropylene and tetrafluoroethylene, such as Viton B sold by DuPont (and similar copolymers sold by 3M as FLUOREL, by Daiken as DAIEL, and by Montefluous as TECHNIFLON), and copolymers of vinylidene fluoride and chlorotrifluoroethylene, such as Kel-F sold by 3M. The use of AFLAS, which is a copolymer of TFE and propylene, as manufactured by Asahi, is also contemplated.

Preferred perfluoroelastomers include elastomeric copolymers of tetrafluoroethylene with perfluoro (alkyl vinyl) comonomers, such as hexafluoropropylene or perfluoro (alkyl vinyl ether) comonomers represented by

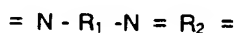


in which  $\text{R}_f$  is a perfluoroalkyl or perfluoro (cyclo-oxa alkyl) moiety. Particularly preferred are the perfluorovinyl ethers in which  $\text{R}_f$  is selected from the groups  $-\text{CF}_3$ ,  $-\text{C}_3\text{F}_7$ ,



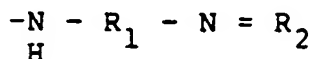
where  $N = 1-4$ ,  $X = \text{H}$ ,  $\text{Na}$ ,  $\text{K}$  or  $\text{F}$ . KALREZ, a copolymer of TFE and perfluoromethylvinyl ether (PMVE), or its modifications, is a particularly useful fluoroelastomer.

The term "polyimide" as used herein encompasses



where  $\text{R}_1$  is a diamide and  $\text{R}_2$  is a dianhydride.

The term polyamide as used herein encompasses



wherein  $\text{R}_1$  and  $\text{R}_2$  have the same meaning as above.

If desired, and as is well-known in the art, fillers or additives such as pigments, plasticizers, stabilizers, softeners, extenders, and the like, can be present in the film composition. For example, there can be present substances such as graphite, carbon black, titanium dioxide, alumina, alumina trihydrate, glass fibers, beads or microballoons, carbon fibers, magnesia, silica, asbestos, wallastonite, mica, and the like.

The fluoropolymer-containing film, which may comprise one or more layers of varying content, is preferably prepared separately. The independent formation of the film permits development of a uniform, low stress, finely metered layer prepared specifically for subsequent application to the substrate. The most preferred technique for preparing the film is casting in preparation for decalcomania transfer or fusion roll

lamination. In such a technique, the film is formed upon a support member which may be any dimensionally stable membrane, such as a metal foil, particularly aluminum foil, or a compatible polymeric film, such as skived PTFE or KAPTON polyimide film. Other techniques for film formation include melt extrusion or coextrusion and calendaring. The lamination of a melt adhesive to the substrate with subsequent coating by the fluoropolymer film is contemplated.

The fluoropolymer-containing film components should preferably be less than 12.7 micrometers (5 mil) thick to result in composites of sufficiently flexibility for use in garments. Preferably such films will be 1-4 mil thick to achieve good protection and flexibility, and most preferably the film is 25.4 - 50.8 micrometers (1-2mil) thick. It is understood that, for substrates laminated on both sides, where high flexibility is unnecessary in the finished article the film used may be of any suitable thickness.

Substrates used according to the invention may be any suitable flexible material capable of withstanding the conditions used to form the laminate. Examples of suitable substrates include, *inter alia*, glass, fiberglass, ceramics, graphite (carbon), PBI (polybenzimidazole), PTFE, polyaramides, such as Kevlar and Nomex, metal such as copper or steel wire, polyolefins such as Tyvek, polyesters such as Reemay, polyamides, polyimides, thermoplastics such as Kynar and Tefzel, polyphenylene sulfide, polyether oxides, polyether sulfones, polyether ketones, novoloid phenolic fibers such as Kynol, cotton, asbestos and other natural as well as synthetic textiles. The substrate may comprise a yarn, filament, monofilament, or other fibrous material either as such or assembled as a textile, or any woven, non-woven such as spun-laced, spun-bonded, or stitch-bonded, or knitted material. The substrate may alternatively comprise a film or paper. No treatment of the fabric is required, although coated fabrics may be employed if desired.

In making the resistant materials of the present invention, an adhesive is used, where necessary, to adhere the substrate to the desired film. A separate adhesive layer need not be used with films which are melt bondable, such as FEP or PFA. The adhesive may be applied to the film layer prior to lamination, or placed between the film and the substrate as a discreet layer and then laminated. Adhesive layers between 2.54 and 38.1 micrometers (0.1 and 1.5 mil) thick are suitable for use in this invention. In the case of woven or knit materials, the substrate may be coated with the adhesive prior to lamination. In the case of nonwoven substrates, coatings of adhesives may lead to a loss of flexibility due to impregnation of the substrate. The composites made according to the present invention avoid this difficulty and remain flexible.

If a melt adhesive is used, it can be fluoropolymer or a non-fluoropolymer, as long as the temperature required for melting is compatible with the laminating film and the substrate fabric. An FEP/Viton adhesive is particularly suitable. Materials which melt at low temperatures, such as TFB (Hoechst), may be used as films and as adhesives. This would allow the use of low melting temperature substrates such as polyolefins, polyesters and polyamides. PFA or PTFE may also be used as the melt adhesive.

In a preferred embodiment, a melt adhesive, preferably FEP/Viton, is applied to a 50.8 micrometer (2 mil) PTFE film for lamination to a fire-resistant substrate such as Nomex SL. The film is heat sealed to the substrate to produce a noncombustible chemically resistant composite.

A layer of PFA, FEP, or other low melting fluorinated polymer or blends thereof may optionally be added to the outside of the film.

The material produced according to this invention is useful for the construction of protective clothing, including hoods, footwear, coveralls, gloves, and supplied air suits. The material may also be used in shelters such as tents, coverings, and as equipment parts where a flexible chemical resistant material is needed.

In constructing the articles, pieces can be joined using any known seaming technique suitable for the end use of the article. A preferred seaming technique for double-sided laminates with melt bondable exterior surfaces according to this invention involves stitching or heat sealing the edges to be joined and then heat sealing the seam to the inside of the garment.

#### Brief Description of the Drawings

Figure 1 is a cross sectional view of a seam for a composite according to this invention during construction.

Figure 2 is a cross-sectional view of a finished seam as shown in construction in Figure 1.

Looking to Figure 1, two pieces, (10) and (12) of composite material to be joined are placed with exterior surfaces (14) and (16) together, and the cut edges (18) and (20) superimposed. A seam is then made, parallel to the cut edges by heat sealing or stitching. The seam allowance (22) is then folded against the interior of the material (24) as shown in Figure 2, and the seam is finally heat sealed. Any stitching used in the seam and the laminate edge are interior and not exposed to challenge agents. The permeation/penetration resistance and the tensile strength of the seamed area are equal to the base

composite.

EXAMPLE 1

5 One side of a cast PTFE 50.8 micrometers (2 mil) film was coated with an adhesive which was a 50/50 blend of a dispersion of a fluoroelastomer (Dupont VTR 5307) and FEP (Dupont TE 9503). The adhesive coating thickness was 12.7 micrometers (.5 mil). The film was laminated to each side of a roll of Nomex Spunlace non-woven (2.7 oz./yd<sup>2</sup> = 0.09 Kg/m<sup>2</sup>) in a continuous laminator having 4 heating zones and 5 pressurized nip rolls. The temperatures and pressures were as follows:

10	Zone	1	2	3	4	5
	Temp (°F)	400	500	550	550	
15	(°C)	204.44	260	282.78	287.78	
	Pressure (psi)	0	5	15	40	50
	= Kg/m <sup>2</sup> x 703					

The laminate's physical properties are in Table 1.

TABLE 1  
Material Physical Property Characterization

PROPERTY	TEST METHOD	EXAMPLE 1	EXAMPLE 2	EXAMPLE 3
Weight (oz/yd) Kg/m <sup>2</sup>	ASTM D751-79	(10.2) 0.345	(6.5) 0.22	(16.9) 0.57
Thickness (mil)micrometer	ASTM D751-79	(15.2) 386	(14.6) 371	(18.4) 467
Tensile Strength	ASTM D751-79	46.0 (W)	19.4 (W)	218.5 (W)
(lbs./in.)Kg/m x 17.8		29.8 (F)	12.5 (F)	184.5 (F)
Tear Strength	ASTM D751-79	(12.4)(W) 5.6	(9.5)(W) 4.3	(18.0)(W)8.16
(lb.) Kg		(6.5)(F) 2.94	(7.5)(F) 3.40	(17.3)(F) 7.8
Bursting Strength	ASTM D751-79	125	102.5	443.3
(psi) Kg/m <sup>2</sup> x 703				
Abrasion Resistance	FED. STD. 191-5302	No loose fibers	No loose fibers	No loose fibers
(after 600 cycles)				
Low Temperature	ASTM D2136-66	Pass	Pass	Pass
Bend (-25°F) -31.67°C				
Flammability	ASTM D568-68	Non-burning	Non-burning	Non-burning

**EXAMPLE 2**

The material produced in Example 1 was subjected to corrosive and hazardous challenge chemicals using the ASTM method F739-81 for permeation and penetration. Other materials were tested for comparison. The results of these tests are shown in Table 2.

In each instance, the laminate according to the present invention showed improved chemical resistance. In addition, the laminate exposed to nitrobenzene showed a substantial improvement in cleanability relative to butyl rubber. Nitrobenzene could be detected in the butyl rubber after cleaning, while in the laminate no nitrobenzene was detectable.

TABLE 2

Chemical	Material	Breakthrough Time
Thionyl Chloride	Example 1 (14 mil) Butyl 355 micrometer	16 hrs.-no breakthrough 53 min. breakthrough
Fuming Nitric Acid 90%	Example 1 SARAN/TYVEK	16 hrs.-no breakthrough 2 hr. breakthrough
Nitrobenzene	Example 1 (14 mil) Butyl 355 micrometer	16 hrs.-no breakthrough 16 hrs.-no breakthrough

**EXAMPLE 3**

The same procedure was followed as in Example 1 except that the film was laminated to one-side of the NOMEX SL. Physical properties of the resulting composite are given in Table 1.

**EXAMPLE 4**

Style 116 glass fabric (greige weight 0.10 Kg/m<sup>2</sup> (3.2 oz./yd<sup>2</sup>)) was coated with two passes of VTR 5307 (Viton) to give a coated weight of 0.18 Kg/m<sup>2</sup> (5.35 oz./yd<sup>2</sup>). Then a coating of a 50/50 FEP/Viton blend was applied to the fabric, followed by a layer of TE 9503 (1.3 g/cm<sup>3</sup>) FEP to give a total weight of 0.215 Kg/M<sup>2</sup> (6.36 oz./yd<sup>2</sup>). This material was laminated to 25.4 micrometer (1 mil) cast PTFE coated with a layer of FEP of approximately 2.54 micrometer (0.1 mil). The static lamination conditions were 510° F for 10 minutes at 70 psi and cooled under pressure.

The resulting composite was tested for chemical permeation and penetration by liquid and gases using ASTM F739-81 method. The results are shown in Table 3.

TABLE 3

Chemical	Material	Breakthrough Time
Bromine	Example 4 Neoprene SAPAN/TYVEK	16 hrs.-no breakthrough 5 min. breakthrough 5 min. breakthrough
65% Fuming Sulfuric	Example 4 (14 mil) Butyl 355 micrometer	16 hrs.-no breakthrough 6 hrs. breakthrough
Nitrobenzene	Example 4 (14 mil) Butyl 355 micrometer	16 hrs.-no breakthrough 16 hrs.-no breakthrough

**EXAMPLE 5**

A composite was laminated of cast fluoropolymer film 60 micrometer (.0024") on both sides of a woven polyaramide substrate (Nomex 0.20 Kg/m 6.0 oz./yd<sup>2</sup>). The cast fluoropolymer film consisted of a 50.8



micrometer (2 mil) film of PTFE coated on one side with a 50/50 FEP/Viton melt adhesive layer 7.6 micrometer (0.3 mil), and on the other side with a layer of PFA (approximately 2.54 micrometer (0.1 mil)). In the lamination, the FEP/Viton melt adhesive side was in contact with the substrate.

Continuous laminator processing conditions were identical to those of Example 1. Physical properties of the resulting composite are shown in Table 1.

Permeation testing was performed by an independent testing organization in accordance with ASTM F731-79 on a battery of 16 challenge agents representing an extremely broad range of chemical families. The challenge agents tested are listed in Table 4. For each chemical tested, the laminated composite according to this invention showed no breakthrough at the end of the eight hour test period.

For comparison, literature values for testing of presently employed resistant materials showing breakthrough by some chemicals during the test period are also given in Table 4.

TABLE 4

Breakthrough Times (min.) of Chemical Protective Clothing Materials (ASTM F739-81)

CHEMICAL	CHEMFAB EXAMPLE 5	SARAN/TYVEK	CPE	VITON/ NEOPRENE	BUTYL NEOPRENE
ACETIC ACID	480+	480+	-	-	-
ACETONITRILE	480+	-	-	45	480+
CARBON DISULFIDE	480+	-	8	-	-
DIETHYLAMINE	480+	44	-	-	-
DIETHYLETHER	480+	-	-	-	-
DIMETHYL FORMAMIDE	480+	-	-	-	-
ETHYL ACRYLATE	480+	-	24	12	60
FREON TF	480+	-	-	-	-
HEXANE	480+	-	-	-	-
METHANOL	480+	-	-	-	-
METHYLE ETHYL KETONE	480+	29	-	480+	480+
NITROBENZENE	480+	-	-	4	5
SODIUM HYDROXIDE	480+	-	62	-	-
SULFURIC ACID (FUMING)	480+	480+	-	-	-
TETRAHYDROFURAN	480+	37	-	480+	480+
TOLUENE	480+	-	12	7	10
		5	-	-	-

-: No Information Available

## 55 EXAMPLE 6

An extruded thermoplastic fluoropolymer (FEP) film 25.4 micrometer (.001") was laminated to one side of a non-woven spunlaced polyaramide fabric. The FEP served as the melt adhesive as well as the film.

Lamination was carried out in the continuous laminator under the following conditions.

Zone	1	2	3	4	5
Temp ( $^{\circ}\text{F}$ )	250	250	450	525	
Temp ( $^{\circ}\text{C}$ )	121.11	121.11	232.22	273.89	
Pressure (psi)	0	5	15	40	50
Pressure ( $\text{kg/m}^2 \times 703$ )					

A flexible composite suitable for use in protective garments was produced.

#### EXAMPLE 7

An extruded thermoplastic fluoropolymer (FEP) film (.001") was laminated to both sides of a non-woven spunlaced polyaramide fabric. The FEP served as the melt adhesive as well as the film. Lamination was carried out in the continuous laminator under the following conditions.

Zone	1	2	3	4	5
Temp ( $^{\circ}\text{F}$ )	250	250	450	525	
Temp ( $^{\circ}\text{C}$ )	121.11	121.11	232.22	273.89	
Pressure (psi)	0	5	15	40	50
Pressure ( $\text{kg/m}^2 \times 703$ )					

A flexible composite suitable for use in protective garments was produced.

#### EXAMPLE 8

Heat sealed seams joining separate pieces of the fluoropolymer/polyaramide composite of Example 1 were made and tested. Figure 1 shows a cross-section of the seam.

In forming the seam, the edges of the composite to be joined were placed together with the extension surfaces touching. The edges were then heat sealed together forming a T-seam. The seam allowance was then folded to lie against the interior of the composite and heat sealed in place.

The seam formed showed chemical resistance and tensile strength equal to the base composites. Results of testing for seam strength and chemical resistance are shown in Table 5.

TABLE 5

Testing of Seam Strength			
Property	Test Method	Seam	Base Composite
Seam Strength (lbs/in) $\text{Kg/m} \times 17.8$	ASTM D 751-79	29.5	29.8
chemical penetration-breakthrough time (min) in fuming nitric acid	ASTM F 739-81	480 +	480 +

#### EXAMPLE 9

A garment was constructed of the fluoropolymer/polyaramide composite described in Example 1. A protection factor of 60,000 was determined using a respirator quantitative fit test. In the test method, a person wearing the garment with an external air supply was placed in a test chamber where the atmospheric environment can be controlled and monitored. A known concentration of a contaminant (aerosol corn oil) was injected into the chamber. A probe on the interior of the garment in the facial region measured the concentration of corn oil which had permeated/penetrated the garment. The concentration at the probe was recorded as the occupant performed several specific exercises. The quantitative fit factor was calculated as the ratio of contaminant concentration in the external environment to the contaminant concentration at the interior probe. The high value indicates that composites according to this invention are suitable for use in protective garments.

EXAMPLE 10

A composite was laminated of cast Teflon film 50.6 micrometers (.002") to one side of a jersey knit polyaramide fabric (Kevlar). Processing conditions were identical to those of Example 1. The composite  
 5 formed was suitable for use in protective garments and afforded better drape, lower resistance to deformation, and improved elasticity when compared to woven and non-woven laminates of comparable thickness.

EXAMPLE 11

10 A composite was laminated of Teflon FEP (TYPE C) to one side of a polyaramide Nomex SL. A solvent-based acrylic interlayer of 33 micrometers (1.3 mil) was employed as the adhesive. The laminate was formed in a static press under light pressure (10 kg/m<sup>2</sup> x 703 = PSI) and ambient temperature. The composite was sewn into a hood assembly which would be appropriate for a self-contained breathing  
 15 apparatus (SCBA) escape respirator. The seams of the article were bound with a tape (1.5 in.) of the same composite.

EXAMPLE 12

20 A double sided laminate was prepared using 1 mil PTFE film under the conditions of Example 1. This was compared with the single sided 50.6 micrometer (2 mil) composite of Example 3 for resistance to fuming nitric acid. The double sided laminate showed no breakthrough in test periods up to 24 hours. The single sided laminate showed breakthrough after 180-200 minutes. Thus, the same total thickness of barrier film is substantially more effective in a double sided composite than in a single sided composite.

Claims

1. A flexible protective article made of a composite comprising a protective layer laminated to one or both  
 30 sides of a flexible substrate, said layers being less than 127 micrometers (5mil) thick and an adhesive applied between the protective layers and the flexible substrate, characterized in that the protective layer is a fluoropolymer containing layer and the adhesive is a melt bondable adhesive having a melt temperature lower than the substrate and the fluoropolymer-containing layers, and selected from the group comprising FEP, FEP alloyed with PTFE, PTFE and PFA.
- 35 2. An article according to claim 1, wherein the melt adhesive is between about 2.54 micrometers (0.1 mil) and 38.1 micrometers (1.5 mil) thick.
3. An article according to claim 1 or 2, wherein the melt adhesive comprises FEP, in particular  
 40 FEP/VITON.
4. An article according to anyone of claims 1 to 3, wherein the same fluoropolymer, selected from the group of FEP and PFA, functions as both the protective layer as well as the adhesive layer.
- 45 5. An article according to claim 4, wherein FEP forms the protective layer as well as the adhesive.
6. An article according to anyone of claims 1 to 5, wherein the protective fluoropolymer-containing layer  
 50 comprises a fluoropolymer selected from the group consisting of polytetrafluoroethylene, fluorinated ethylene propylene, copolymer, perfluoroalkoxy resin, homopolymers of polychlorotrifluoro-ethylene, copolymers of polychlorotrifluoroethylene with trifluoroethylene or vinylidene fluoride, ethylene-chlorotrifluoroethylene copolymer, ethyl ne tetrafluoroethylene copolymer, polyvinylidene fluoride and polyvinyl fluoride.
7. An article according to anyone of claims 1 to 6, wherein the substrate comprises a flexible material  
 55 selected from the group consisting of glass, fiberglass, ceramics, graphite, polybenzimidazole, polytetrafluoroethylene, polyaramides, metal, polyolefins, polyesters, polyamides, polyimides, thermoplastics, polyphenylene sulfide, polyether oxides, polyether sulfones, polyether ketones, novoloid phenolic fibers, cotton, and asbestos, said flexible material being woven, nonwoven or knitted.

8. An article according to anyone of claims 1 to 7, additionally comprising a layer of melt adhesive applied to the outer surface of the fluoropolymer-containing layer.

9. An article according to claim 8, wherein the fluoropolymer-containing layers are 25.4 - 50.8 micrometers (1-2 mil) thick.

10. An article according to claim 9, wherein the outer melt adhesive is a polyfluoroalkoxy resin.

11. Use an article according to any of the preceding claims as clothing, shelter or covering.

12. A method of preparing of a flexible protective article made of a composite comprising casting a film of a protective-containing material said film being about 127 micrometers (5 mil) or less thick and laminating the film to one or both sides of a flexible substrate, subsequent to placing an adhesive between the protective film and the flexible substrate, characterized in that it is selected a protective layer containing a fluoropolymer, the adhesive is applied as an adhesive layer and is a melt bondable adhesive having a melt temperature lower than the substrate and the fluoropolymer-containing layers, and selected from the group comprising FEP, FEP alloyed with PTPE, PTFE and PFA.

13. A method according to claim 12, wherein the layer of adhesive is cast onto the fluoropolymer-containing film prior to lamination.

14. A method according to claims 12 or 13, wherein lamination is accomplished using pressure and heat.

#### Patentansprüche

1. Aus einem Schichtstoff hergestellter flexibler Schutzgegenstand, bei dem auf eine oder beide Seiten eines flexiblen Trägermaterials eine Schutzschicht laminiert ist, wobei diese Schichten weniger als 127  $\mu\text{m}$  (5 mil) dick sind und zwischen den Schutzschichten und dem flexiblen Träger ein Klebstoff angeordnet ist, dadurch gekennzeichnet, daß die Schutzschicht eine ein Fluoropolymer enthaltende Schicht ist und der Klebstoff ein Schmelzklebstoff ist, dessen Schmelztemperatur niedriger als die des Trägers und der ein Fluoropolymer enthaltenden Schichten ist und der ausgewählt ist aus der aus FEP, FEP im Gemisch mit PTFE, TFB, PTFE und PFA bestehenden Gruppe.

2. Gegenstand nach Anspruch 1, worin der Schmelzklebstoff zwischen etwa 2,54  $\mu\text{m}$  (0,1 mil) und 38,1  $\mu\text{m}$  (1,5 mil) dick ist.

3. Gegenstand nach Anspruch 1 oder 2, worin der Schmelzklebstoff FEP, insbesondere FEP/VITON ist.

4. Gegenstand nach einem der Ansprüche 1 bis 3, worin das gleiche Fluoropolymer, das aus der Gruppe FEP und PFA ausgewählt ist, sowohl als Schutzschicht als auch als Klebstoffschicht wirkt.

5. Gegenstand nach Anspruch 4, worin FEP die Schutzschicht und auch den Klebstoff bildet.

6. Gegenstand nach einem der Ansprüche 1 bis 5, worin die ein Fluoropolymer enthaltende Schutzschicht ein Fluoropolymer umfaßt, das ausgewählt ist aus der Gruppe, die besteht aus Polytetrafluorethylen, fluorierten Copolymerisaten von Ethylen und Propylen, Perfluoralkoxyharz, Homopolymerisaten von Polychlortrifluorethylen, Copolymerisaten von Polychlortrifluorethylen und Trifluorethylen oder Vinylidenfluorid, Copolymerisaten von Ethylen und Chlortrifluorethylen, Copolymerisaten aus Ethylen und Tetrafluorethylen, Polyvinylidenfluorid und Polyvinylfluorid.

7. Gegenstand nach einem der Ansprüche 1 bis 6, worin das Trägermaterial ein flexibles Material umfaßt, das ausgewählt ist aus der Gruppe, die besteht aus Glas, Glasfasern, Keramik, Graphit, Polybenzimidazol, Polytetrafluorethylen, Polyaramiden, Metallen, Polyolefinen, Polyestern, Polyamiden, Polyimiden, Thermoplasten, Polyphenylensulfid, Polyetheroxiden, Polyethersulfonen, Polyetherketonen, Novoloid-Phenolfasern, Baumwolle und Asbest, wobei dieses flexible Material gewoben, nicht gewoben oder gewirkt ist.

8. Gegenstand nach einem der Ansprüche 1 bis 7, dadurch gekennzeichnet, daß er zusätzlich eine Schicht aus einem Schmelzklebstoff enthält, die auf die äußere Oberfläche der in Fluorpolymer enthaltenden Schicht aufgebracht ist.
- 5 9. Gegenstand nach Anspruch 8, worin die ein Fluorpolymer enthaltenden Schichten 25,4 bis 50,8 µm (1 bis 2 mil) dick sind.
10. Gegenstand nach Anspruch 9, worin der äußere Schmelzklebstoff ein Polyfluoralkoxyharz ist.
- 10 11. Verwendung eines Gegenstands nach einem der vorhergehenden Ansprüche als Bekleidung, Schutzdecke oder Umhüllung.
12. Verfahren zur Herstellung eines aus einem Schichtstoff hergestellten flexiblen Schutzgegenstands durch Gießen eines Films aus einem ein Schutzmittel enthaltenden Material, wobei dieser Film etwa 15 127 µm (5 mil) oder weniger dick ist, und Laminieren des Films auf eine oder beide Seiten eines flexiblen Trägermaterials, nachdem zwischen dem Schutzfilm und dem flexiblen Trägermaterial ein Klebstoff angeordnet worden ist, dadurch gekennzeichnet, daß als Schutzschicht eine ein Fluorpolymer enthaltende Schicht ausgewählt wird, der Klebstoff als Klebstoffschicht aufgetragen wird und ein 20 Schmelzklebstoff ist, dessen Schmelztemperatur niedriger als die des Trägermaterials und der ein Fluorpolymer enthaltenden Schichten ist und der ausgewählt ist aus der aus FEP, FEP im Gemisch mit PTFE, TFB, PTFE und PFA bestehenden Gruppe.
13. Verfahren nach Anspruch 12, worin die Klebstoffschicht vor der Laminierung auf den ein Fluorpolymer enthaltenden Film gegossen wird.
- 25 14. Verfahren nach Anspruch 12 oder 13, worin die Laminierung unter Anwendung von Druck und Hitze vorgenommen wird.

# Revendications

- 30 1. Un article protecteur flexible réalisé en un composite comprenant une couche protectrice stratifiée sur un ou sur deux côtés d'un substrat flexible, lesdites couches étant inférieures à 127 µm (5 mil) d'épaisseur et un adhésif appliqué entre les couches protectrices et le substrat flexible, caractérisé en ce que la couche protectrice est une couche contenant un polymère fluoré et l'adhésif est un adhésif 35 susceptible d'être lié par fusion ayant une température de fusion inférieure à celle du substrat et des couches contenant le polymère fluoré, et choisi dans le groupe comprenant le FEP, le FEP allié avec le PTFE, le TFB, le PTFE et le PFA.
2. Un article selon la revendication 1, selon lequel l'adhésif par fusion a une épaisseur comprise entre 40 environ 2,54 µm (0,1 mil) et 38,1 µm (1,5 mil).
3. Un article selon la revendication 1 ou 2, selon lequel l'adhésif par fusion comprend du FEP, en particulier du FEP/MITON.
- 45 4. Un article selon l'une quelconque des revendications 1 à 3, selon lequel le même polymère fluoré, choisi dans le groupe comprenant le FEP et le PFA, agit à la fois comme couche protectrice et comme couche adhésive.
- 50 5. Un article selon la revendication 4, selon lequel le FEP forme la couche protectrice en même temps que l'adhésif.
- 55 6. Un article selon l'une quelconque des revendications 1 à 5, selon lequel la couche protectrice contenant le polymère fluoré comprend un polymère fluoré sélectionné dans le groupe comprenant les suivants : polytétrafluoroéthylène, copolymère d'éthylène-propylène fluoré, résine perfluoroalcoxy, homopolymères de polychlorotrifluoroéthylène, copolymères de polychlorotrifluoroéthylène avec le trifluoroéthylène ou le fluorure de vinylidène, copolymère d'éthylène-chlorotrifluoroéthylène, copolymère d'éthylène-tétrafluoroéthylène, fluorure de polyvinylidène et fluorure de polyvinyle.

7. Un article selon l'une quelconque des revendications 1 à 6, selon lequel le substrat comprend un matériau flexible choisi dans le groupe comprenant les suivants : verre, fibre de verre, céramique, graphite, polybenzimidazol, polytétrafluoroéthylène, polyaramides, métal, polyoléfines, polyesters, polyamides, polyimides, thermoplastiques, sulfure de polyphénylène, oxydes de polyéther, polyéther-sulfones, polyéthercétone, fibres phénoliques novoloïdes, coton, et amiante, ledit matériau flexible étant tissé, non tissé ou tricoté.
8. Un article selon l'une quelconque des revendications 1 à 7, comprenant additionnellement une couche d'adhésif par fusion appliquée à la surface extérieure de la couche contenant un polymère fluoré.
9. Un article selon la revendication 8, selon laquelle les couches contenant le polymère fluoré ont une épaisseur de 25,4-50,8  $\mu\text{m}$  (1-2 mil).
10. Un article selon la revendication 9, selon lequel l'adhésif par fusion extérieure est une résine polyfluoroalcoxy.
11. Utilisation d'un article selon l'une quelconque des revendications précédentes comme article d'habillement, article de protection ou article de couverture.
12. Une méthode de préparation d'article protecteur flexible réalisé en un composite comprenant la coulée d'un film d'un matériau contenant un protecteur, ledit film ayant une épaisseur d'environ 127  $\mu\text{m}$  (5 mil) ou moins et la stratification du film sur un ou sur deux côtés d'un substrat flexible, caractérisée en ce que l'on choisit une couche protectrice contenant un polymère fluoré, l'adhésif est appliqué sous la forme d'une couche adhésive et est un adhésif susceptible d'être lié par fusion ayant une température de fusion inférieure à celle du substrat et des couches contenant le polymère fluoré, et choisi dans le groupe comprenant le FEP, le FEP allié avec le PTFE, le TFB, le PTFE et le PFA.
13. Une méthode selon la revendication 12, selon laquelle la couche d'adhésif est coulée sur le film contenant le polymère fluoré avant la stratification.
14. Une méthode selon la revendication 12 ou 13, selon laquelle la stratification est réalisée en utilisant la pression et la chaleur.

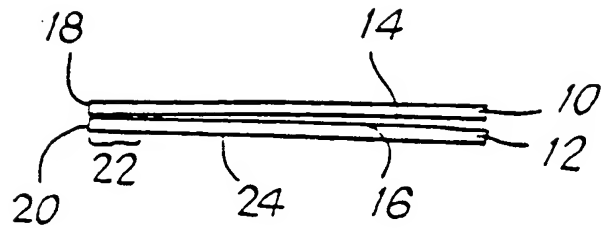


Fig. 1

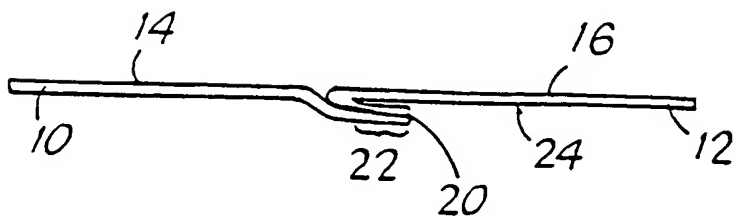


Fig. 2